

# ADHESIVE TAPE AND PROCESS FOR REMOVING RESIST

## Background of the Invention

### 1. Field of the Invention

5           The present invention relates to an adhesive tape or sheet  
(hereinafter simply referred to as "adhesive tape") for use  
in the removal of unnecessary resist material from  
precision-machined parts as semiconductor, thin film magnetic  
head, circuit, print circuit board, mask and lead frame during  
10 the production of these precision-machined parts and a process  
for the removal of a resist using this adhesive tape.

15           The invention will be described hereinafter with  
reference to production of semiconductor device. The invention  
is not limited to its usage so far as the article to which it  
is applied has a resist material present thereon. However,  
the invention is preferably used particularly in the removal  
of unnecessary resist material from the wafer after plating  
or etching during the production of semiconductor device.

### 2. Description of the Related Art

20           In the process for the production of semiconductor device,  
a resist material is applied to a silicon wafer. The silicon  
wafer is then subjected to an ordinary photographic process  
to form a predetermined resist film image thereon. The silicon  
wafer is then etched with this resist film image as a mask.

25           The unnecessary resist material was then removed to form a

predetermined circuit. Subsequently, in order to form another circuit, a resist material is again applied to the silicon wafer. This cycle is repeated. In the case where a circuit is formed on any other various substrates (boards), too, the formation of a resist film image is followed by the removal of unnecessary resist material.

The removal of unnecessary resist material is normally accomplished by the use of a solvent and a chemical. However, there is a problem that the use of harmful chemicals deteriorates the working atmosphere and it requires a troublesome environmental measure to dispose the waste liquid. In particular, the plating step in the formation of various bumps involves the use of a resist material having a thickness as great as from about 20  $\mu\text{m}$  to 120  $\mu\text{m}$  that needs much time to be removed with a large amount of a chemical. The remaining of the resist after the removal of the chemical, too, causes a problem.

A method has thus been recently proposed which comprises sticking adhesive tape made of a high molecular polymer to the upper surface of a resist film image, subjecting the material to a specific treatment such as heat treatment, and then peeling the adhesive tape and the resist material integrally (as in Japanese Patent Laid-Open No. 1992-345015).

However, the method involving the use of such an adhesive tape is disadvantageous in that peeling cannot be fairly effected

depending on the kind of the resist to be peeled. In particular, when the thickness of the resist film exceeds 10  $\mu\text{m}$ , the resist can be often difficultly peeled with the conventional adhesive tape for the removal of a resist.

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### Summary of the Invention

An object of the invention is to allow even a resist material having such a thickness to be fairly peeled.

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The inventors made extensive studies of solution to these problems. As a result, it was found that peeling can be easily effected under heating conditions and the use of an adhesive tape having an adhesive layer which maintains a high elasticity even under heating conditions after cured makes it possible to improve the peelability of the resist. It was further found that the use of an adhesive tape comprising such an adhesive layer provided on a supporting base material having a high flexural stiffness makes it possible to further improve the peelability of the resist.

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The invention lies in an adhesive tape for the removal of a resist comprising a curing adhesive layer (i.e., an adhesive layer to be subjected to curing) provided on a supporting base material, the curing adhesive layer exhibiting an initial tensile modulus of not smaller than 10 MPa at 100°C after cured, an adhesive tape for the removal of a resist comprising an adhesive layer provided on a supporting base material having a flexural stiffness of not smaller than  $1 \times 10^{-4}$  (N·m) per unit

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width, an adhesive tape for the removal of a resist comprising  
in combination the adhesive layer and the supporting base  
material, a process for the removal of a resist which comprises  
applying an adhesive tape to an article on which a resist film  
5 image is present, and then peeling off the adhesive tape and  
the resist film image together from the article, and the process  
for the removal of a resist according to the invention, wherein  
peeling is effected under conditions of heating to a temperature  
of not lower than 50°C.

#### 10 Detailed Description of the Invention

In the invention, an example of the article on which a  
resist material is present is one obtained by a process which  
comprises applying a known resist material to an article such  
as semiconductor substrate (board) and glass substrate (board),  
15 subjecting the coated article to an ordinary photographic  
process to form a predetermined resist pattern thereon, and  
then subjecting the article to a processing such as metal plating  
and etching on the opening thereof with this resist material  
as a mask. In the case where the article is subjected to metal  
20 plating, a negative-working liquid resist or dry film resist  
is preferably formed to a thickness of from 10  $\mu\text{m}$  to 150  $\mu\text{m}$   
in most cases. The resist material having such a thickness  
cures when irradiated with ultraviolet rays during patterning  
and thus can difficultly be peeled off together with a tape  
25 at room temperature.

However, since the resist material which has cured is thermoplastic, it becomes soft and exhibits a deteriorated adhesivity to the substrate when heated. Thus, the resist material can be easily peeled off from the substrate. The peeling temperature depends on the resist material to be peeled but is normally from 50°C to 200°C, preferably from 80°C to 150°C. However, since the adhesive incorporated in an ordinary adhesive tape for the removal of a resist becomes plasticized under these heating conditions similarly to the resist material, the peeling stress can be difficultly transferred to the surface of the resist material, making it impossible to fairly peel off the resist material from the substrate. It was found that this problem can be solved by the use of a material which maintains a high elasticity even under heating conditions as an adhesive layer. In this arrangement, the peeling stress can be concentrated onto the resist material, giving good results in peeling. It was thus found that the use of an adhesive tape having an adhesive layer which exhibits an initial tensile modulus of not smaller than 10 MPa, preferably from about 20 MPa to 200 MPa at 100°C after cured makes it possible to fairly peel off the resist material from the substrate.

The adhesive tape to be used herein is in the form of a sheet or tape comprising an adhesive layer provided on a supporting base material normally to a thickness of from 20  $\mu\text{m}$  to 150  $\mu\text{m}$ . The surface of the supporting base material is

normally subjected to physical surface treatment such as corona discharge or undercoating with an adhesivity-providing layer for the purpose of securing adhesivity to the adhesive layer.

In order to allow the adhesive layer to fairly follow the

5 unevenness on the substrate during sticking, an interlayer made

of various polymers such as acrylic polymer and rubber-based polymer or a pressure-sensitive adhesive mainly composed of

these polymers may be provided interposed between the supporting

base material and the adhesive layer for the removal of a resist

10 to a predetermined thickness. The supporting base material

to be used herein is not specifically limited. For example,

a plastic film made of a polyethylene, polypropylene,

polyethylene terephthalate, acetyl cellulose or the like having

a thickness of normally from 25  $\mu\text{m}$  to 500  $\mu\text{m}$  is preferably used.

15 A supporting base material having a great flexural stiffness

is particularly preferred. In some detail, the supporting base

material preferably exhibits a flexural stiffness of not smaller

than  $1 \times 10^{-4}$  (N·m), more preferably from not smaller than  $5$

$\times 10^{-4}$  to not greater than  $1 \times 10^{-1}$  (N·m), per unit width. The

20 use of such a supporting base material makes it possible to

peel off the resist material from the substrate more uniformly.

The term "flexural stiffness" as used herein is meant to indicate

the degree of difficulty for an object in being deformed due

to bending as referred to in the art of materials dynamics.

25 The flexural stiffness is represented by the product of the

tensile modulus E and the second moment of area I of the film.  
The flexural stiffness is proportional to the third power of  
the thickness of the film to be bent and can be determined by  
calculation if the kind and shape of the film are determined  
5 (see Equation 1).

$$\text{Flexural stiffness} = E(\text{N/m}^2) \times I(\text{m}^4) \text{ (Eq. 1)}$$

where  $I = 1/12 \times b \times h^3$  (b: width of film to be bent; h: thickness  
of film to be bent)

10 The adhesive layer to be used herein is not specifically  
limited. A curing adhesive which cures to become integrated  
to the resist material when irradiated with light or otherwise  
treated is preferably used. In particular, a photo-setting  
adhesive comprising a photopolymerizable compound and a  
photopolymerization initiator incorporated in an acryl polymer  
15 is preferably used.

As such a polymer there may be used any known polymer  
which can be used in pressure-sensitive adhesives. From the  
standpoint of development of high elasticity during heating,  
it is preferred that the polymer comprise a methacrylic acid  
20 alkyl ester in a proportion of not smaller than 50% by weight  
based on the total composition. This methacrylic polymer can  
be obtained by allowing a methacrylic acid alkyl ester and an  
acrylic acid alkyl ester as main monomers to undergo ordinary  
polymerization such as solution polymerization, emulsion  
25 polymerization, suspension polymerization and bulk

polymerization with a carboxyl group or hydroxyl group-containing monomer or other reactive functional group-containing monomers. The molecular weight of the methacrylic polymer formed by these monomers is preferably from 10,000 to 1,500,000, particularly from 30,000 to 300,000 as calculated in terms of weight-average molecular weight.

As such a polymerizable compound there may be used one which can cure when provided with light or thermal energy, preferably a photosetting compound. Such a compound is a nonvolatile compound having one or more unsaturated double bonds which can cure when irradiated with light. The amount of the photopolymerizable compound to be used is preferably from not smaller than 10 parts by weight to not greater than 200 parts by weight based on 100 parts by weight of the high molecular polymer.

Examples of such a polymerizable compound include phenoxy polyethylene glycol (meth)acrylate,  $\epsilon$ -caprolactone (meth)acrylate, polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol hexa(meth)acrylate, urethane (meth)acrylate, epoxy (meth)acrylate, and oligoester (meth)acrylate. One or more of these polymerizable compounds may be used. In order to enhance the elasticity of the adhesive layer during heating after cured, one or more of these polymerizable compounds to be used each have three or four



unsaturated double bonds per molecule. As the polymerization initiator, particularly photopolymerization initiator there may be mainly used a compound which generates a radical when irradiated with light such as ultraviolet rays, such as  
5 benzylmethyl ketal, benzoin, dibenzyl, thioxanthone compound and benzoin ethyl ether.

In order to reduce the content of low molecular components in the adhesive after cured and hence improve the cohesive force of the adhesive, the adhesive may comprise a polyfunctional compound such as polyfunctional epoxy compound, polyisocyanate compound and aziridine compound incorporated therein in a proper amount. The adhesive may further comprise various additives such as tackifier, colorant and age resistor incorporated therein so far as the effect of the invention cannot be impaired.

15 The best embodiment of the invention is an adhesive tape for the removal of a resist comprising a curing adhesive layer having an initial tensile modulus of not smaller than 10 MPa at 100°C after cured provided on a supporting base material having a flexural stiffness of not smaller than  $1 \times 10^{-4}$  (N·m)  
20 per unit width as defined above.

The process to which the process for the removal of a resist of the invention is not specifically limited. In particular, however, the process for the removal of a resist of the invention can be employed in the process for the production  
25 of precision-machined parts such as semiconductor, thin film

magnetic head, circuit, print circuit board, mask and lead frame.  
Accordingly, the invention provides a process for the production  
of various precision-machined parts including at least such  
a process for the removal of a resist and a precision-machined  
5 part produced by such a process for the removal of a resist  
such as semiconductor, thin film magnetic head, circuit, print  
circuit board, mask and lead frame.

The invention will be further described in the following  
examples. The resist film image A to be peeled in the examples  
10 has been formed on a semiconductor wafer by the method described  
in Reference Example 1.

#### REFERENCE EXAMPLE 1

An electrode portion for connection to the exterior and  
an insulating portion were formed on the surface of a silicon  
15 wafer on which a semiconductor element had been formed. A  
negative-working dry film resist (thickness: 120  $\mu\text{m}$ ) was then  
stuck to the surface of the silicon wafer. The silicon wafer  
was then subjected to ordinary exposure and development to form  
a pattern thereon. Thereafter, the silicon wafer was  
20 copper-plated on the surface thereof with this resist pattern  
as a mask to a thickness of 110  $\mu\text{m}$ . The image pattern thus  
formed on the silicon wafer is referred to as "resist film image  
A".

#### EXAMPLE 1

25 200 g of a 35% toluene solution of Acryl Polymer A

(weight-average molecular weight: 110,000; weight-average molecular weight (Mw)/number-average molecular weight (Mn) = 2) made of a 40/25/25/10 (by weight) copolymer of methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and acrylic acid which had been synthesized by an ordinary method and a toluene solution of 10 g of a polyethylene glycol 400 diacrylate (NK Ester A-400, produced by Shinnakamura Chemical Co., Ltd.), 10 g of a trimethylolpropane triacrylate (A-TMPT, produced by Shinnakamura Chemical Co., Ltd.), 10 g of tetramethylolmethane triacrylate (A-TMM3, produced by Shinnakamura Chemical Co., Ltd.), and 2 g of benzyldimethyl ketal (Irgacure 651, produced by Ciba Specialty Chemicals Co., Ltd.) were applied to a polyester supporting film (N100G50, produced by Mitsubishi Chemical Polyester Film Co., Ltd.; flexural stiffness per unit length:  $4.2 \times 10^{-5}$  (N·m)) having a thickness of 50  $\mu\text{m}$ , and then each dried at a temperature of 130°C in a drying oven for 3 minutes to form an adhesive layer thereon to a thickness of 50  $\mu\text{m}$ . Thus, an adhesive tape for the removal of a resist was prepared. The adhesive layer thus obtained exhibited an initial tensile modulus (Young's modulus) of 32 MPa at 100°C after cured.

Subsequently, the adhesive tape thus obtained was stuck to the resist film image A on the semiconductor wafer under heating to 100°C under a pressure roller. The adhesive tape was then irradiated with ultraviolet rays from a high voltage

mercury vapor lamp at a dosage of 1 J/cm<sup>2</sup> to become cured. Thereafter, the adhesive tape and the image A were together peeled off from the wafer to remove the image A from the wafer. The semiconductor wafer was then visually observed to have been  
5 fully freed of resist material. However, a resist material residue having a thickness as small as scores of micrometers was observed in the vicinity of the border of the undercoat layer with the copper plate column under microscope.

#### EXAMPLE 2

10 A curing adhesive tape for the removal of a resist was prepared in the same manner as in Example 1 except that as the supporting film there was used a polyester film (A4100, produced by TOYOBO CO., LTD.; flexural stiffness per unit length: 6.5  
15 x 10<sup>-4</sup> (N·m)) having a thickness of 125 μm. The resist film image A was peeled off from the wafer in the same manner as in Example 1. The semiconductor wafer was then visually observed to have been fully freed of resist material. No resist material residue was observed even under microscope.

#### EXAMPLE 3

20 A curing adhesive tape for the removal of a resist was prepared in the same manner as in Example 1 except that 100 g of a 20% toluene solution of Acryl Polymer B (weight-average molecular weight: 820,000; weight-average molecular weight (Mw)/number-average molecular weight (Mn) is nearly equal to  
25 4) made of a 85/15/3 (by weight) copolymer of n-butyl acrylate,

acrylnitrile and acrylic acid which had been synthesized by an ordinary method and a toluene solution of 6 g of an urethane acrylate (U-N-01, produced by Shinnakamura Chemical Co., Ltd.), 0.6 g of an isocyanate crosslinking agent (Colonate L, produced by NIPPON POLYURETHANE INDUSTRY CO., LTD.) and 0.6 g of benzylmethyl ketal (Irgacure 651, produced by Ciba Specialty Chemicals Co., Ltd.) were used as adhesive solutions. The adhesive layer thus obtained exhibited an initial tensile modulus (Young's modulus) of 2.5 MPa at 100°C after cured. The resist film image A was peeled off from the semiconductor wafer in the same manner as in Example 1. The semiconductor wafer was then visually observed to have been fully freed of resist material. However, a resist material residue having a thickness as small as scores of micrometers was observed in the vicinity of the border of the undercoat layer with the copper plate column under microscope.

#### COMPARATIVE EXAMPLE 1

The adhesive solution as used in Example 3 was applied to the supporting film having a thickness of 50  $\mu\text{m}$  as used in Example 1 to prepare a photosetting adhesive tape for the removal of a resist having a thickness of 50  $\mu\text{m}$ . The resist film image A was peeled off from the wafer in the same manner as in Example 1. As a result, little or no resist material was removed. An interfacial exfoliation occurred between the adhesive tape and the surface of the resist material.

## COMPARATIVE EXAMPLE 2

The resist film image A was peeled off from the substrate in the same manner as in Example 3 except that the temperature of the substrate during peeling was the same as room temperature.

5 As a result, no resist material was removed from the substrate.

In accordance with the invention, the initial tensile modulus of the adhesive layer which has cured is predetermined to a high value and/or the flexural stiffness of the supporting base material is enhanced. In this arrangement, the peeling stress can be concentrated onto the surface of the resist material, enabling uniform peeling. Accordingly, a process for assuring the removal of the resist material, particularly one having a great thickness, can be provided.

This application is based on Japanese patent application  
15 JP 2001-020946, filed January 30, 2001, the entire content of which is hereby incorporated by reference, the same as if set forth at length.